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Studies on Heat and Mass Transfer Limitations in Oxidative Dehydrogenation of Ethane over Cr_2O_3 /Al_2O_3 Catalyst

P.Thirumal bai[a], V.Manokaran[a], P.S.Saiprasad[b], S.Srinath[a]*

[a]*Department Chemical Enineering, National Institute of Technology Warangal,INDIA*
[b]*Inorganic & Physical Chemistry Division, Indian Institute of Chemical Technology,Hyderabad, INDIA.*

Abstract

In heterogeneous catalytic reactions the heat and mass transfer play a vital role in affecting the rate of a reaction. Mass transfer limitations include both the internal and external diffusion of components into and out of the catalyst while heat transfer limitations include whether the reaction taking place is isothermal in nature and to find maximum temperature within the catalyst particle during the course of reaction. In the study of intrinsic rates of reaction both the diffusion mechanism should be negligible prior to the kinetic studies. Oxidative dehydrogenation of ethane over Cr_2O_3 /Al_2O_3 using CO_2 as oxidant was investigated in a fixed bed reactor. The order of reaction is considered to be One and the internal and external diffusion is studied by Weisz Prater and Mears criteria. Temperature difference with in the catalyst particle computed to check the heat transfer limitations.

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Keywords: Oxidative dehydrogenation; Ethane;CO_2;Weisz prater criteria;Mears criteria;Diffusion

1. Introduction

Ethylene is one of the important compounds in building block off petrochemical industry. Traditionally ethylene is produced by steam cracking and catalytic cracking of ethane and naphtha. These production methods has several disadvantages such as consuming large amount of energy due to endothermic nature of reaction, coke formation,

* Corresponding author. Tel.: +918702462624;
E-mail address: srinath@nitw.ac.in

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thermodynamic constraints, inefficient selectivity control [1,2,3]. ODH of ethane using O_2 as oxidant has higher ethane conversion but the selectivity of ethylene is very low because of the formation of secondary oxidation products such as CO, CO_2.ODH of ethane using CO_2 as a mild oxidant reduces the formation of above mentioned products as CO_2 acts as a catalytic poison for non selective sites of catalyst [4,5] which leads to formation of those products. Also the reverse water gas shift reaction aids in the formation of ethylene by dehydrogenation of ethane.

$$H_2 + CO_2 \rightarrow CO + H_2O$$

Supported chromium catalysts are highly active for ODH of ethylene and it offers superior ethane and CO_2 conversion. $Cr_2O_3/ZSM\text{-}5$ [6], Cr_2O_3/Al_2O_3, Cr_2O_3/SiO_2, Cr_2O_3/ZrO_2, Cr_2O_3/TiO_2 [7], modified Cr_2O_3/ZrO_2 nano-composites [8], $Cr/SBA\text{-}15/Al_2O_3/FeCrAl$ monoliths [9], Cr-O, Cr-V-O oxide [10], catalysts have been used for oxidative dehydrogenation of ethane in presence of the soft oxidant CO_2. Chromium containing Ga_2O_3 catalysts supported on HZSM-5 and silicalite [11] are also found to be active for this reaction. However, gallium based catalysts offer low conversion of the light alkane and CO_2 and undergoes drastic deactivation within a few hours on stream. The catalyst used in our study is Cr_2O_3/Al_2O_3 with CO_2 as oxidant in a fixed bed reactor.

Diffusion of reactants into the catalyst play vital role while determining the kinetics of the reaction. Prior to kinetic studies it is important to study the diffusion of reactants from the bulk phase to the surface of the catalyst particle, and subsequently from the surface to the inside of the particle. Internal and external diffusion play a major role in the transfer rate of reactants to heterogeneous catalysts. In this study the effects of these two resistances and effect of heat transfer were investigated for ethane oxidative dehydrogenation on Cr_2O_3/Al_2O_3 catalyst.

Nomenclature

R	radius of catalyst particle
N_A	Mass flux of A
$D_{A,mix}$	Diffusivity of A in gas mixture
D_e	Effective diffusivity
C_{Ab}	Bulk concentration of gas A
C_{Ac}	Concentration of A at the centre of catalyst
C_{As}	Concentration of A at the surface of catalyst
C_A	Exit concentration of A
ϕ_1	Thiele modulus
ϕ	Porosity of bed
σ	Constriction Factor
τ	Tortuosity
ρ_c	Catalyst density
ρ_b	Catalyst Bulk density
λ_{eff}	Effective thermal conductivity of catalyst
λ_s	Thermal conductivity of solid
λ_f	Thermal conductivity of fluid
η	Effectiveness factor
C_{wp}	Weisz prater parameter
$-r_A'$	Rate of the reaction per unit weight of catalyst
C_m	Mears parameter
$-\Delta H_r$	Heat of the reaction
k_1''	Rate constant per unit surface area of catalyst
S_a	Surface area of catalyst

2. Materials and Methods

2.1 Catalyst Preparation

Commercially available alumina (Al_2O_3, Sud Chemie Ind. Pvt. Ltd) support was used in this work. The catalysts with 5-20 wt% Cr_2O_3 on Al_2O_3 were prepared by adopting conventional wet impregnation method. The procedure was as follows. The required quantity of $Cr(NO_3)_3.9H_2O$ was dissolved in minimum amount of water and this solution was added to the Al_2O_3 support with constant stirring. Excess water was removed on a water bath, and the catalyst masses were dried in an air oven at 120 °C for 12 h. Finally, 5-20 wt% Cr_2O_3 supported alumina catalysts were obtained by calcination at 650 °C for 6 h.

2.2 Catalyst Performance

Catalyst evaluation was carried out in a fixed-bed stainless steel reactor at atmospheric pressure. In each catalytic run, about 1 g of catalyst (particles of 18/25 mesh size) diluted with equal amount of quartz beads, was suspended between two quartz wool plugs at the center of the reactor. Prior to reaction the catalyst was pretreated in helium flow (30 ml/min) at 500 °C for 1 h. Ethane, carbon dioxide and helium were fed into the reactor at a volume ratio of 15/15/30 using mass flow controllers (Alborg, USA) and maintaining the bed temperature with a PID controller. The effluent gas stream was analyzed by an on-line Nucon 5765 GC equipped with TCD using Molecular sieve 5A and Porapak Q columns.

3. Catalyst Characterization Results

3.1 *Temperature programmed reduction profiles of the catalysts*

Temperature programmed reduction (TPR) was performed in a flow of 5% H_2/Ar mixture gas at a flow rate of 30 ml/min with a temperature ramp of 10 °C/min.The TPR profiles of alumina supported chromium catalysts with varying loadings (5-20 wt%) calcined at 650 °C/6h are given in Fig.2. Only single stage reduction was exhibited by all the catalysts in the range between 379 to 415 °C. It was been reported in the literature [12,13] that the single stage reduction occurs due to the reduction of Cr^{+6} to Cr^{+3}, as per the following reaction:

$$2\,CrO_3 + 3H_2 \rightarrow Cr_2O_3 + 3H_2$$

5 wt% Cr_2O_3/Al_2O_3 catalyst showed the reduction temperature (T_{max}) centered at 415 °C. This value shifted towards lower temperature (379 °C) when the content of Cr_2O_3 increased to 15 wt% and remained constant above 15 wt% loading, these results are in good agreement with the earlier reports [12,13,14].

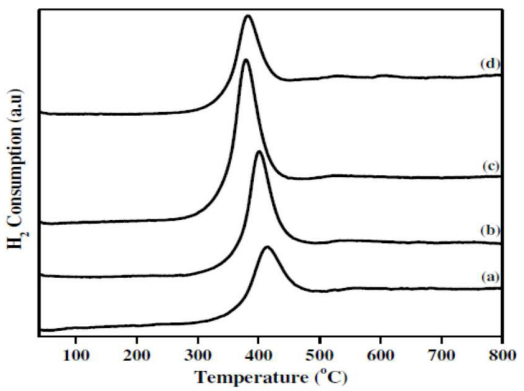

Fig.1. TPR profiles of catalysts calcined at 650 ºC/ 6h (a) 5% Cr_2O_3/Al_2O_3, (b) 10% Cr_2O_3/Al_2O_3, (c) 15% Cr_2O_3/Al_2O_3 and (d) 20% Cr_2O_3/Al_2O_3

At lower loadings oxygen is strongly bound to the support due to strong chromium-support interactions. It requires higher temperature for reduction, whereas in higher loadings chromium-support interactions become weaker due to the accumulation of chromia. They consume hydrogen comparatively at lower temperatures to undergo reduction [13,14]. Zaki et al [15] described the reduction behavior of chromium coated alumina catalysts. The chromium can be stabilized in two different kinds of species; polychromates and monochromates. The polychromate species exposed on crystalline chromia reduce at lower temperatures and the monochromate species directly anchored to the support reduce at higher temperatures.

4. Effect of temperature

The effect of temperature on conversions of ethane and CO_2 at optimum loading (15 wt% Cr_2O_3/Al_2O_3) of catalyst is shown in Fig 2.The conversion of ethane and CO_2 both increases with increase in temperature up to 600 °C and there is a small variation from 600 to 650 °C. The selectivity of ethylene also follows the same trend as conversion with respect to temperature up to 600 °C and remains constant till 650 °C. The redox cycles of Cr^{+6} to Cr^{+3} may increase with rise in temperature might be responsible to attain high catalytic activity at 650 °C

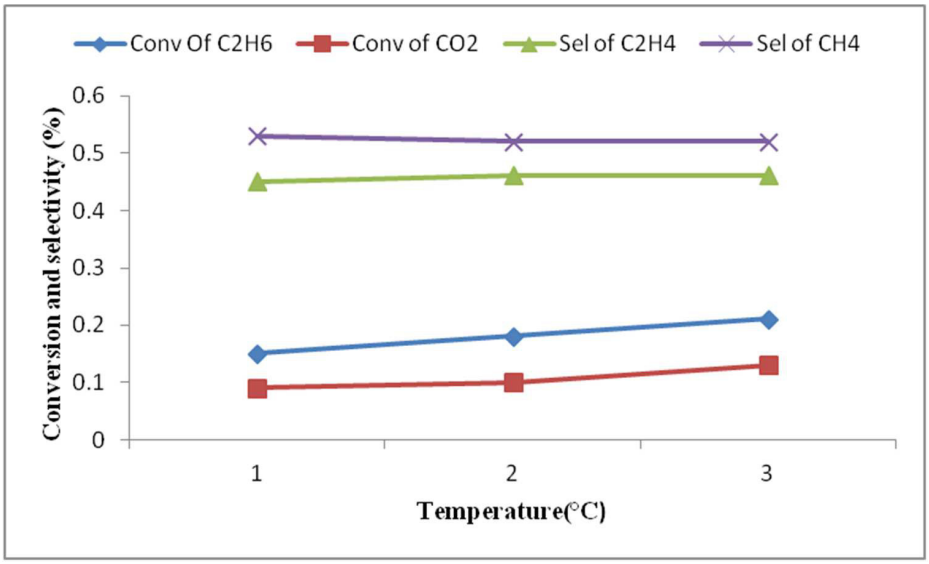

Fig 2.Effect of temperature on catalytic activity of 15 wt% Cr_2O_3/Al_2O_3 in ODH of Ethane with CO_2

5. Diffusion Effects on Heterogeneous reactions

In heterogeneous catalytic reactions the diffusion of gas from the bulk to catalyst surface (External diffusion) and from the surface to the interior of catalyst (Internal diffusion) plays an important role in rate of reaction. These diffusion mechanism act as resistances which affects the rate of reaction and it should be neglected. The figure below gives the steps taking place in a porous catalytic particle

5.1 Internal diffusion

For a spherical catalyst particle of radius R in which first order reaction takes place at steady state the mass balance for A is given by

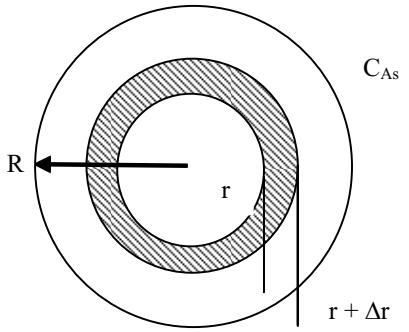

Fig 3.Shell Balance on a catalyst pellet

Shell mass balance on catalyst Pellet:

[$Rate\ of$ mass A in] - [Rate of mass A out] + [Rate of disappearance of A within the element Δr] = 0

$$[4\pi R^2 N_A]_r - [4\pi R^2 N_A]_{r+\Delta r} + [-r_A' \rho_c 4\pi R^2 \Delta r] = 0$$

$$\frac{d(N_A r^2)}{dr} - r_A' \rho_c r^2 = 0 \quad (1)$$

The molar flux of A by molecular diffusion is given by

$$N_A = -D_e \frac{dC_A}{dr} \quad (2)$$

where D_e is effective diffusivity given by

$$D_e = \frac{D_{AB}\,\phi\,\sigma}{\tau} \quad (3)$$

Where D_{AB} is the bulk or Knudsen diffusivity of A in B, ϕ is the pellet porosity and σ is the constriction factor. The σ value is taken as 1 for many cases and the tortuosity [16] of catalyst is calculated from porosity by

$$\tau = 1 - 0.5 ln\phi \quad (4)$$

Thiele modulus ϕ_1 of 1st reaction order is given by

$$\phi_1 = \frac{surface\ reaction\ rate}{diffusion\ rate} = R\sqrt{\frac{k_1'' S_a \rho_c}{D_e}} \quad (5)$$

If thiele modulus is very high the mass transfer controls the reaction and if it is low then surface reaction is the rate limiting step. The internal effectiveness factor η can also be used to check whether internal diffusion is the rate limiting step. The internal effectiveness factor depends on reaction order as well as catalyst shape. For a first order reaction on a spherical catalyst the internal effectiveness factor is given by [17]

$$\eta = \frac{3}{\phi_1^2}(\phi_1 \coth\phi_1 - 1) \quad (6)$$

The internal effectiveness factor η is nearly equal to 1 when internal diffusion in the catalyst is negligible.

Weisz Prater criterion [17] is used to check whether the reaction is diffusion limited .

$$C_{wp} = \frac{-r'_A \rho_c R^2}{D_e C_{As}} < 1 \quad (7)$$

C_{wp} =Actual reaction rate/A diffusion rate

The Internal diffusion equation is negligible when C_{wp} is <<1 and vice versa
The values to be used in the above equation is given in the table below

Table 1. Parameters values for calculating Weisz prater criteria

Parameters	Values
r_A'(obs)	$3.26*10^{-7}$ (mol/Kg $_{cat}$.s)
ρ_c	500 (Kg/m^3)
R	225 (µm)
D_e	$2.33*10^{-5}$(m^2/s)
C_{As}	$3.25*10^{-3}$ (mol/lit)
Φ	0.78
τ	**1.1**

The value of C_{wp} is equal to 0.0001 on substitution of the above values and from this we can infer that internal diffusion is negligible in the above reaction.

5.2 External Diffusion

Under steady state conditions the external diffusion of the reactants into heterogeneous catalyst from bulk of fluid is equal to the rate at which reactants are consumed both within the catalyst and the surface. Mears Criterion [18] is used to check whether the reaction is limited by external diffusion which is given below

$$C_m = \frac{-r'_A \rho_b R n}{K_C C_{Ab}} < 0.15 \quad (8)$$

Since the Reynolds number is very low creeping flow of fluid exists and the mass transfer coefficient [19] is calculated from the correlation (Sh-Sherwood number)

$$\mathrm{Sh} = (4 + 1.21\ \mathrm{Pe}^{\frac{2}{3}})^{1/2} \quad (9)$$

Where Pe is the Pectlet number, Pe = Reynolds number (Re)* Schmidt number (Sc). For calculation of Re and Sc the various properties of gases are found from [20],[21].

From which mass transfer coefficient K_c is given by

$$K_c = \frac{D_{A,mix} Sh(1-\phi)}{d_p\, \phi} \quad (10)$$

Table 2. Parameters values for estimating Mears criteria

Parameters	Values
r_A'	$3.26*10^{-7}$ (mol/Kg cat.s)
ρ_c	500 (Kg/m^3)
R	225 (µm)
n	1
Φ	0.78

C_{Ab}	3.25*10-^{3} (mol/lit)
K_c	0.109 (m^3/m^2.s)

The value of C_m is $2.25*10^{-4} < 0.15$ so the external diffusion of gases into the catalyst is negligible

6. Heat Transfer effects in the catalyst

Since oxidative dehydrogenation of ethane using CO_2 is endothermic in nature, non isothermal effects in the catalyst is much lesser as the particle is cooler than the surrounding fluid when compared with exothermic reactions. Temperature difference ΔT within the catalyst particle is given by Prater for any particle geometry and kinetics. Laplace equation is used to represent both temperature and concentration within the particle and hence their corresponding distribution curves must have the same shape at any point in the pellet x.

$$-\lambda_{eff}\frac{dT}{dx} = -D_e\frac{dC_A}{dx}(-\Delta H_r) \tag{11}$$

Where λ_{eff} is the effective thermal conductivity
- ΔH_r is the heat of the reaction

The effective thermal conductivity λ_{eff} [22] is in turn calculated by

$$\lambda_{eff} = \lambda_s^{1-\phi}\lambda_f^{\phi} = \lambda_s\left(\frac{\lambda_f}{\lambda_s}\right)^{\phi} \tag{12}$$

The value of λ_{eff} is found to be 0.2178 W/m.K

For the catalyst pellet as a whole is given by

$$\Delta T_{Particle} = \frac{D_e(C_{As}-C_{A,centre})}{\lambda_{eff}} \tag{13}$$

The ΔT within the particle is nearly equal to zero so the catalytic reaction is isothermal in nature

7. Conclusions

In this study, the diffusion effects were investigated for the ethane dehydrogenation reaction over Cr_2O_3/Al_2O_3 catalyst. The value of Mear's criterion shows the importance of mass transfer resistance over a catalyst. With regard to the results for the catalyst with C_m = 0.00022, the external mass transfer is very much negligible at the given operating conditions. The Thiele modulus value decreases as size of catalyst particle decreases and the effectiveness factor tends to a value nearly equal to 1.For a effectiveness factor value equal to 1 the internal diffusion is negligible. Also the external diffusion is negligible at the operating feed flow rate and hence both diffusion resistances are negligible. As the effectiveness factor approaches 1 the surface reaction is said to be the controlling mechanism and from the heat transfer studies the reaction is found to be isothermal in nature.

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